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Asymmetric Aryl Polyhedral Oligomeric Silsesquioxanes (ArPOSS) with Enhanced Solubility

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Abstract

Four new asymmetric Polyhedral Oligomeric Silsesquioxanes (POSS) with the formula (Aryl)Phenyl₇Si₈O₁₂, where Aryl = 1-naphthyl, 2-naphthyl, 9-phenanthrenyl, and 1-pyrenyl, have been synthesized in reasonable yield and high purity. These compounds were characterized with ¹H, ¹³C, ²⁹Si NMR and elemental combustion analysis. These compounds possess polycyclic aromatic functionality, which disrupts symmetry to improve solubility in organic solvents and aromatic polymers, without significant impact on thermal stability.

1. Introduction

The synthesis of hybrid organic-inorganic materials that combine the diversity and ease of processing of organic polymers with the thermo-chemical stability and oxidative resistance of ceramics remains a goal of material researchers worldwide. Polyhedral Oligomeric Silsesquioxanes (POSS) have emerged as effective multi-functional, highly tailorable additives, capable of improving polymer performance [1-4]. Each of these nanoparticles features an inorganic SiO_{1.5} core, as well as an organic corona, which helps to determine overall solubility. Compounds based on this architectural framework have received a great deal of attention as

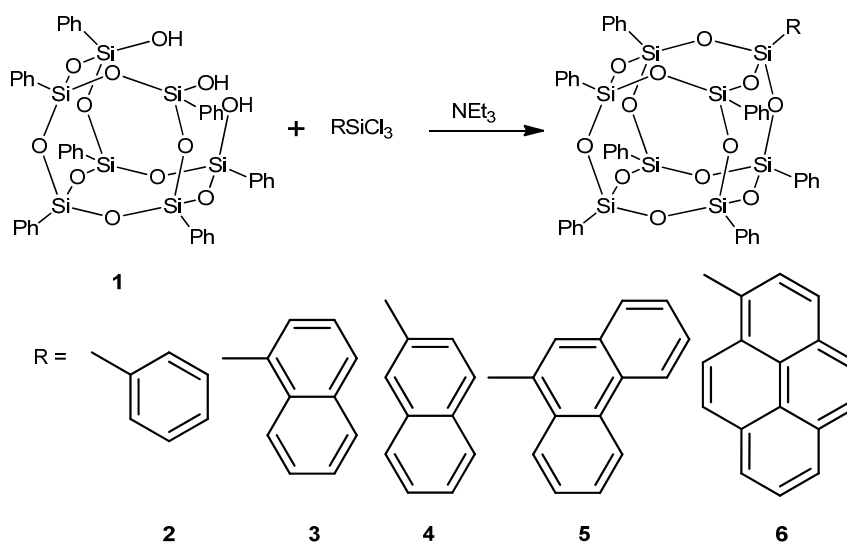
nearly ideal hybrid materials due to the synergy of the silsesquioxane cage and organic character at the molecular level [5]. In contrast to most other forms of nanoscale reinforcement, POSS compounds have been shown to improve processing characteristics when either blended into polymer hosts or incorporated by copolymerization [6-10]. Although both techniques have distinct advantages, inert blending is generally the preferred method, offering facile modification of commercial polymers without the necessity for polymer synthesis and balancing stoichiometry. Furthermore, blending techniques generally provide access to a greater material design space in the context of nanoparticle assembly. However, the availability of thermally stable, inert POSS additives for the purpose of reinforcing high temperature polymers by this method is limited. Further development would be of benefit to a range of potential products requiring lightweight materials for energy efficiency, aerospace, and durable infrastructure applications.

Aryl-functionalized silsesquioxanes, such as phenyl $_8\text{Si}_8\text{O}_{12}$ ($\text{Ph}_8\text{Si}_8\text{O}_{12}$), have been in existence for decades, appearing well-suited for the preparation of high-performance, aromatic nanocomposites [11-15]. However, the high symmetry and low dipole moments of $\text{Ph}_8\text{Si}_8\text{O}_{12}$ promote highly-efficient crystalline packing. This is manifested in poor solubility in organic solvents, and a neutral response to mechanical shear, thus severely limiting incorporation into polymers [16, 17]. To circumvent these limitations, several research groups have focused on the modification of aryl-functionalized POSS compounds. For example, Sellinger *et al.* functionalized vinyl $_8\text{Si}_8\text{O}_{12}$ with aromatic photo-luminescent compounds *via* Heck coupling [18, 19]. Laine *et al.* reported the synthesis of (*para*-iodophenyl) $_8\text{Si}_8\text{O}_{12}$ as a platform for coupling additional organic moieties to POSS cages [20]. Their work highlighted the ability to produce soluble symmetric POSS cages. Other work by Shi *et al.* attached $\text{Ph}_8\text{Si}_8\text{O}_{12}$ to

polybenzimidazole *via* an *in-situ* Friedel-Crafts acylation copolymerization reaction [21]. They found that copolymerized $\text{Ph}_8\text{Si}_8\text{O}_{12}$ was more thoroughly dispersed in the polymer host than physically blended $\text{Ph}_8\text{Si}_8\text{O}_{12}$. Herein, we report the synthesis of aromatic POSS compounds, *via* a “corner-capping” methodology, which overcomes the limitations of $\text{Ph}_8\text{Si}_8\text{O}_{12}$ through geometric consideration of the POSS cage periphery. These compounds demonstrate enhanced solubility in organic solvents and aromatic polymers, enabling a more facile route to the fabrication of high temperature nanocomposites.

2. Results and Discussion

Aromatic POSS structures were synthesized by the “corner-capping” of phenyl $\gamma\text{-Si}_7\text{O}_9(\text{OH})_3$ (**1**) with aryl trichlorosilanes. The desired aryl trichlorosilanes were synthesized by reaction of an aryl Grignard or lithium reagent with SiCl_4 under reaction conditions similar to those previously reported [22]. The aryl trichlorosilanes (ArSiCl_3) (Ar = phenyl, 1-naphthyl, 2-naphthyl, 9-phenanthrenyl, and 1-pyrenyl) were coupled with **1** under basic conditions to yield the desired, well-defined (Aryl)phenyl $\gamma\text{-Si}_8\text{O}_{12}$ structures (Scheme 1).



Scheme 1. Synthesis of corner capped POSS cages.

The desired products of these reactions were separated from byproducts and starting materials *via* filtration and methanol washings. Previous work has proven this synthetic strategy as an effective technique at coupling trichlorosilanes to silanols [10, 23-25]. These POSS cage structures were confirmed on the basis of multinuclear NMR (^1H , ^{13}C , and ^{29}Si) and elemental combustion analysis (CHN). The absence of silanol NMR peaks was used to confirm reaction completion. The initial chemical shifts of the ^{29}Si NMR peaks for **1** are -69.08, -77.54, and -78.51 ppm, respectively, in a ratio of 3:1:3. For comparison, the chemical shift of the single peak for symmetric phenyl $_8\text{Si}_8\text{O}_{12}$ (**2**) is -78.07 ppm. When the corner-capping reaction is complete on the asymmetric compounds, the ^{29}Si NMR peaks are shifted with respect to the additional substituent aryl group. For example, the peaks of (1-naphthyl)phenyl $_7\text{Si}_8\text{O}_{12}$ (**3**) are shifted to -77.37, -78.05, -78.14, and -78.17 ppm, respectively, in a ratio of 1:3:1:3 (Figure 1). Similar peak shifts in ^{29}Si NMR spectra were observed for the remaining corner-capped compounds, though the order of peak integration is occasionally different.

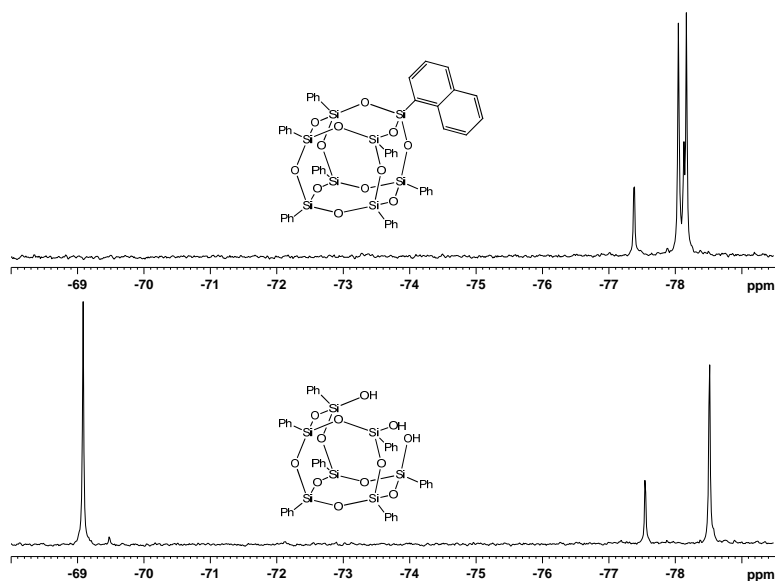


Figure 1. ^{29}Si NMR spectra of **1** (bottom) and **3** (top).

The influence of the prescribed peripheral asymmetry of these compounds on solubility was determined by visual measurements in five organic solvents, including chloroform (CHCl_3), tetrahydrofuran (THF), phenyl ether (PE), toluene (Tol), and dimethyl formamide (DMF), and is summarized in Table 1. The poor solubility of **2** has been previously documented [17], exhibiting only limited solubility ($\sim 1 \text{ mg/mL}$) in CHCl_3 and thus, serving as the benchmark for this work. As expected, the substitution of a single polycyclic aromatic ring on the POSS cage improves solubility substantially in most cases. However, it is difficult to predict the influence of each aromatic group on the observed solubility, as well as in which solvent the solubility will be affected. Modification with a 1-naphthyl group to produce **3** results in solubility in CHCl_3 and THF exceeding 100 mg/mL and the observation of more finite solubility in the other investigated solvents. Modification with a 2-naphthyl group to produce (2-naphthyl)phenyl $_7\text{Si}_8\text{O}_{12}$ (**4**) increases solubility in PE and DMF, but reduces solubility in THF and CHCl_3 , when compared to **3**. Substitution with a phenanthrenyl group to produce (9-phenanthrenyl)phenyl $_7\text{Si}_8\text{O}_{12}$ (**5**) results in comparable solubility in THF to that of **2**, as well as the highest solubility in DMF and toluene of any compound examined. Limited solubility gains in comparison with the other polycyclic aromatic groups are observed with pyrenyl substitution, with (1-pyrenyl)phenyl $_7\text{Si}_8\text{O}_{12}$ (**6**) exhibiting the lowest solubility of the four corner-capped POSS cages in the examined solvents, albeit a noteworthy improvement over that of **2**.

Table 1. Solubility (mg/mL) of aromatic POSS compounds in organic solvents.

| # | CHCl_3 | THF | PE | Tol | DMF |
|----------|-----------------|--------------|--------------|-----------------|--------------|
| 2 | 1 | ^a | ^a | ^a | ^a |
| 3 | 104 | 120 | 15 | ^a 24 | |
| 4 | 55 | 28 | 53 | ^a 35 | |
| 5 | 52 | 117 | 25 | 27 | 57 |
| 6 | 7 | 10 | 4 | 5 | 5 |

^aInsoluble.

To examine the phase behavior of this new class of asymmetric POSS nanoparticles with a representative aromatic polymer, attempts were made to solubilize both **2** and **3** in polyetherimide (Ultem 1000, PEI). Chloroform solutions were prepared at a solute concentration of 5 weight percent PEI and POSS concentration of 5 weight percent with respect to PEI. Subsequent films from these solutions were drop cast onto glass substrates, dried under vacuum, and annealed at 220 °C, above the glass transition temperature of PEI, to promote equilibrium phase formation. The overall results of this study are depicted in Figure 2. In accordance with the solubility study, the solution containing asymmetric **3** is transparent, indicating superior solubility in chloroform, in contrast to that containing **2**, which is cloudy.

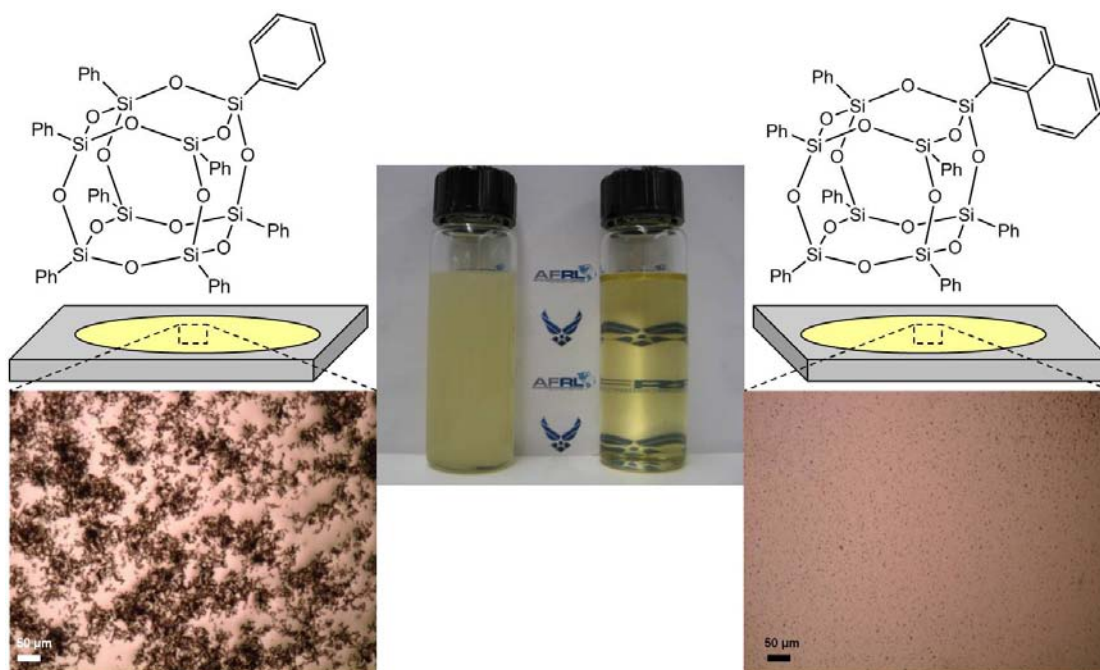


Figure 2. Inside: Photographs of PEI solutions containing **2** (left) and **3** (right) in chloroform . Outside: Optical micrographs of drop cast films from solutions containing **2** (left) and **3** (right).

Qualitatively, the dried and annealed films were visually observed to be of contrasting appearance. The film containing **2** was significantly more opaque, suggesting a greater degree of phase separation. Examination of the films by microscopy revealed aggregated particles of **2** at length scales greater than 1 μm in some regions of the PEI host. Phase separation in the film containing **3** appears to be limited to less than 5 μm in the post-annealed state, revealing improved solubility in the predominately aromatic polymer.

In order to examine the thermal stability of compounds **2-6**, thermogravimetric analysis (TGA) was conducted on 5-10 mg samples in a nitrogen atmosphere at a scan rate of 10 $^{\circ}\text{C}/\text{minute}$. The results of this study are summarized in Table 2. In comparison with **2**, each of these compounds exhibits a lower temperature, corresponding to a 5% weight loss. The temperature trend appears to decrease with geometric size of the corner cap group, ranging from a reduction of 7% for **3** to 17% for **6**. A detailed description of the thermal properties of these compounds in relation to chemical architecture will be provided in a subsequent publication.

Table 2. Five percent weight loss temperatures ($^{\circ}\text{C}$) of aromatic POSS compounds in nitrogen measured by TGA.

| 2 | 3 | 4 | 5 | 6 |
|----------|----------|----------|----------|----------|
| 465 | 432 | 406 | 399 | 385 |

3. Conclusions

Replacing a single phenyl ring on **2** with one of several polycyclic aromatic groups results in compounds that exhibit improved solubility in organic solvents and aromatic polymers, without significant sacrifices in thermal stability. These improvements, relative to the state-of-the-art materials, are realized through a disruption of symmetry and reduced ordering in the forms of crystallization and/or aggregation. Frameworks containing a single unique pendant group were prepared and isolated. These compounds offer new opportunities to

blend ArPOSS with a variety of organic/polymer materials, a possibility that was previously impractical due to the insolubility of **2**. Future work will focus on the influence of soluble ArPOSS compounds on polymer nanocomposite properties.

4. Experimental

4.1 Materials

Phenyl₇Si₇O₉(OH)₃ was obtained from Hybrid Plastics, while additional silicon-containing organic compounds were purchased from Gelest. Remaining chemicals were purchased from Aldrich. All chemicals were used without further purification unless otherwise noted. All reactions were performed under an atmosphere of dry nitrogen. Flasks were oven-dried and allowed to cool under nitrogen prior to use.

4.2 Characterization

¹H, ¹³C, and ²⁹Si NMR spectra were obtained on Bruker 300-MHz and 400-MHz spectrometers using 5 mm o.d. tubes. Sample concentrations were approx. 10% (w/v) in chloroform-*d*. Combustion analysis was performed by Atlantic Micro Lab, Inc. Norcross, GA. Thermogravimetric analysis (TGA) was performed on a TA Instruments Q5000 using 5-10 mg of material, at a scan rate of 10 °C/minute under a nitrogen atmosphere.

4.3 General synthesis of chlorosilane compounds

4.3.1 1-Naphthyltrichlorosilane

Under a dry nitrogen atmosphere, a solution of 1-bromonaphthalene (27.7 g, 0.134 mol) in THF (175 mL) was added slowly to a suspension of magnesium turnings (3.9 g, 0.16 mol) in THF (15 mL) that had previously been activated with an iodine crystal. After cooling to room temperature, this Grignard reagent was added via canula to a SiCl₄ (25.1 g, 0.148 mol) THF (70 mL) solution and stirred overnight. The mixture was evaporated to dryness, extracted with

hexane and filtered to remove Mg halide. The product was distilled at 120 °C under dynamic vacuum to give a 67% yield (23.6 g, 0.0902 mmol) of product. ^1H NMR (CDCl_3 , ppm) 8.46 (dd, 1H), 8.21 (dd, $J=6.8$ Hz, $J=1.2$ Hz, 1H), 8.09 (d, $J=8.4$ Hz, 1H), 7.96 (d, $J=7.6$ Hz, 1H), 7.69 (t, 1H), 7.62 (t, 1H), 7.57 (t, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 135.51 (CH), 134.42 (C), 134.07 (CH), 133.58 (C), 129.37 (CH), 127.91 (C), 127.45 (CH), 127.16 (CH), 126.56 (CH), and 124.65 (CH). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -0.17 (s).

4.3.2 2-Naphthyltrichlorosilane

Yield 31%. ^1H NMR (CDCl_3 , ppm) 8.40 (s, 1H), 7.96 (d, 2H), 7.89 (d, 1H), 7.82 (dd, $J=8.4$ Hz, $J=1.5$ Hz, 1H), 7.62 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 135.49 (CH), 135.06 (C), 132.28 (C), 128.90 (CH), 128.54 (C), 128.52 (CH), 128.34 (CH), 127.85 (CH), 127.34 (CH), and 127.02 (CH). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -0.87 (s).

4.3.3 9-Phenanthrenyltrichlorosilane

Yield 58%. ^1H NMR (CDCl_3 , ppm) 8.76 (m, 1H), 8.68 (d, $J=8.4$ Hz, 1H), 8.48 (s, 1H), 8.43 (m, 1H), 7.99 (dd, $J=7.9$ Hz, $J=0.5$ Hz, 1H), 7.75 (m, 3H), 7.67 (t, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 139.02 (CH), 132.30 (C), 131.36 (C), 130.48 (C), 130.10 (CH), 129.77 (C), 129.45 (CH), 128.18 (CH), 127.25 (CH), 127.19 (CH), 127.14 (CH), 126.77 (C), 123.49 (CH), and 122.56 (CH). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -0.51 (s).

4.3.4 1-Pyrenyltrichlorosilane

Under a dry nitrogen atmosphere, *n*-BuLi (10.6 mL, 1.6 M) in hexanes was added dropwise to a cooled (-60 °C) solution of 1-bromopyrene (5.01 g, 0.018 mmol) in THF/Et₂O (1:1) (80 mL) and stirred for 2 hours at -60 °C. The solution was cooled to -90 °C and a THF solution of SiCl₄ (8.66 g, 0.051 mmol) (10 mL) was added slowly and stirred for 24 hours at room temperature. The reaction mixture was evaporated to dryness, washed in Et₂O (100 mL), and filtered to

remove any unreacted 1-bromopyrene and LiBr. The filtrate was collected and evaporated to dryness to give a 48% yield of 1-trichlorosilylpyrene a yellow powder. ^1H NMR (CDCl_3 , ppm) 8.66 (d, $J=9.3$ Hz, 1H), 8.59 (d, $J=8.1$ Hz, 1H), 8.30 (m, 5H), 8.11 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 136.18 (C), 135.85 (C), 133.13 (CH), 132.06 (C), 131.30 (C), 131.22 (CH), 130.31 (CH), 127.96 (CH), 127.67 (CH), 127.61 (CH), 126.65 (CH), 125.61 (C), 125.01 (CH), and 124.39 (C). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -1.64 (s).

4.4 General synthesis of POSS compounds

4.4.1 (1-Naphthyl)phenyl Si_8O_{12} (1-NapPh Si_8O_{12}) (3)

Under a dry nitrogen atmosphere, phenyl $\text{Si}_7\text{O}_9(\text{OH})_3$ (19.0 g, 0.0211 mol) was dissolved in THF (150 mL). A solution of 1-naphthyltrichlorosilane (5.63 g, 0.0215 mol) in THF (50 mL) was then slowly added. A dilute solution of triethylamine (6.84 g, 0.0676 mol) in THF (100 mL) was then added over a 90 minute period under vigorous stirring. The reaction was allowed to proceed overnight. The solution was then filtered and the volume reduced under dynamic vacuum. The product was dissolved in ether and an aqueous wash (4:1) was performed to remove water-soluble byproducts. The solution was again reduced under vacuum and the remaining oil was dissolved in THF. The solution was precipitated in methanol and then filtered to obtain a 92% yield of product (21.0 g, 0.0194 mol). ^1H NMR (CDCl_3 , ppm) 8.51 (m, 1H - nap), 8.04 (dd, $J=6.8$ Hz, $J=1.3$ Hz, 1H - nap), 7.98 (d, $J=8.3$ Hz, 1H - nap), 7.81 (m, 15H - nap/ph), 7.39 (m, 24H - nap/ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 136.45 (C - nap), 135.36 (CH - nap), 134.22, 134.21, 134.18 (3:1:3, CH - ph), 133.16 (C - nap), 131.51 (CH - nap), 130.83, 130.80, 130.77 (3:1:3, CH - ph), 130.17, 130.13, 130.03 (3:1:3, C - ph), 128.65 (CH - nap), 128.34 (CH - nap), 128.23 (C - nap), 127.91, 127.88, 127.85 (3:1:3, CH - ph), 126.50 (CH -

nap), 125.73 (CH - nap), and 124.83 (CH - nap). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -77.37, -78.05, -78.14, and -78.17 (1:3:1:3). Combustion Anal. (Calcd): C, 57.68 (57.64); H, 3.81 (3.91).

4.4.2 (2-Naphthyl)phenyl Si_8O_{12} (2-NapPh Si_8O_{12}) (4)

Yield 90%. ^1H NMR (CDCl_3 , ppm) 8.31 (s, 1H - nap), 7.84 (m, 18H - nap/ph), 7.45 (m, 23H - nap/ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 135.91 (CH - nap), 134.51 (C - nap), 134.22 (CH - ph), 132.59 (C - nap), 130.82, 130.80 (3:4, CH - ph), 130.14 (C - ph), 129.58 (CH - nap), 128.46 (CH - nap), 127.89 (CH - ph), 127.71 (CH - nap), 127.47 (C - nap), 127.29 (CH - nap), 127.06 (CH - nap), and 126.03 (CH - nap). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -77.94, -78.14, and -78.18 (1:3:4). Combustion Anal. Calcd): C, 57.28 (57.64); H, 3.87 (3.91).

4.4.3 (9-Phenanthrenyl)phenyl Si_8O_{12} (PhenPh Si_8O_{12}) (5)

Yield 79%. ^1H NMR (CDCl_3 , ppm) 8.74 (d, $J=7.6$ Hz, 1H - phen), 8.68 (d, $J=8.3$ Hz, 1H - phen), 8.51 (dd, $J=7.8$ Hz, $J=1.2$ Hz, 1H - phen), 8.31 (s, 1H - phen), 7.84 (m, 15H - phen/ph), 7.64 (m, 4H - phen), 7.43 (m, 21H - ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 138.35 (CH - phen), 134.24, 134.23 (3:4, CH - ph), 133.89 (C - phen), 131.66 (C - phen), 130.83 (CH - ph), 130.59 (C - phen), 130.18, 130.14, 130.03 (3:1:3, C - ph), 129.97 (C - phen), 129.21 (CH - phen), 127.91, 127.88 (3:4, CH - ph), 127.11 (C - phen), 126.86 (CH - phen), 126.60 (CH - phen), 126.43 (CH - phen), 122.92 (CH - phen), and 122.40 (CH - phen). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -77.28, -78.06, -78.12, and -78.18 (1:3:3:1). Combustion Anal. (Calcd): C, 59.10 (59.33); H, 3.84 (3.91).

4.4.4 (1-Pyrenyl)phenyl Si_8O_{12} (PyPh Si_8O_{12}) (6)

Yield 29%. ^1H NMR (CDCl_3 , ppm) 8.72 (d, $J=9.2$ Hz, 1H - py), 8.43 (d, $J=7.6$ Hz, 1H - py), 8.21 (m, 2H - py), 8.12 (m, 3H - py), 8.04 (m, 2H - py), 7.80 (m, 14H - ph), 7.37 (m, 21H - ph). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , ppm) 136.09 (py - C), 134.29, 134.24 (3:4, CH - ph), 133.34 (py -

C), 133.30 (py - CH), 131.14 (py - C), 130.87, 130.81 (4:3, CH - ph), 130.74 (py - C), 130.24, 130.20, 130.10 (3:1:3, C - ph), 128.66 (py - CH), 128.11 (py - CH), 127.95, 127.91 (3:4, CH - ph), 127.78 (py - CH), 127.47 (py - CH), 125.91 (py - CH), 125.59 (py - CH), 125.42 (py - CH), 125.27 (py - C), 124.60 (py - C), 124.50 (py - C), and 124.04 (py - CH). $^{29}\text{Si}\{^1\text{H}\}$ (CDCl_3 , ppm) -76.80, -77.82, and -77.93 (1:3:4). Combustion Anal. (Calcd): C, 59.77 (60.18); H, 3.75 (3.83).

Acknowledgement

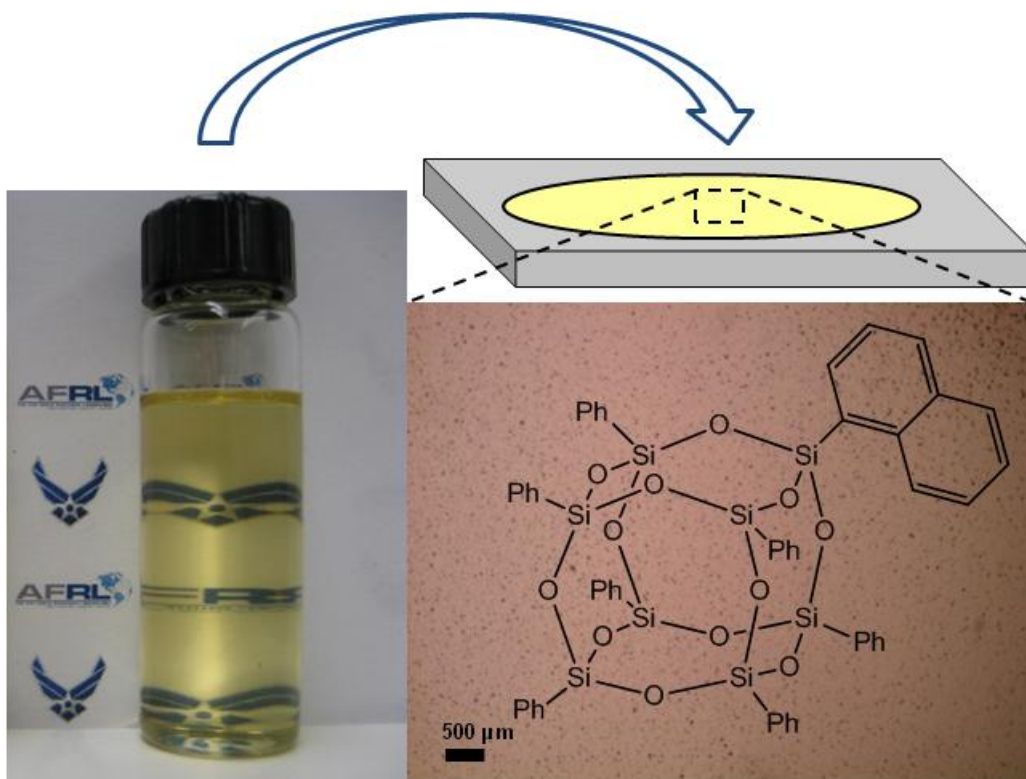
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Table of Contents Image



Solution cast optical micrograph of Aryl POSS in polyetherimide on glass slide.

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Asymmetric Aryl Polyhedral Oligomeric Silsesquioxanes (ArPOSS) with Enhanced Solubility

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Graphical Abstract: Pictogram

